Adverse effects of pollution on mankind: Ground water Fluoride and its Removal

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***Abstract*: Pollution is one of the most horrible ecological crises of the environment to which we are subjected today. Pollution is unfavorable alternation of the environment, largely because of human activities and it is usually brought by the addition of waste products to the environment. Pollutants are biotic and physical component which adversely alters the environment by altering the growth rate of species. Pollutants is a substance which has a potential to induce cancer, or Neoplastic effects, or to induce a permanent transmissible change in the characteristic, if they are exposed via respiratory tract, skin, eyes, mouth or any other routes in quantity which are reasonable to them. Fluoride is a major worldwide pollutant; it is atoxic substance which readily enters the body and has a wide range of systematic effects. Fluoride occurs in all water supplies. It may present in detrimental concern in ground water. Fluoride concentration up to 1ppm is considered to be beneficial in water but excessive fluoride in drinking water may cause mottling of teeth or dental fluorosis. Fluorosis is a permanent damage to the enamel which consist of white or brown spots that appear on the children teeth. Fluoride contents were determined by SPADNS method. Defluoridation is done by HAGG method and its derivatives.**

Index Terms: Pollution, pollutants, Neoplastic effects, Fluorosis, SPADNS, HAGG Method.

I. INTRODUCTION

"Environmental chemistry" is the science of chemical phenomenon occurring in the environment. It is a multibranched science involving chemistry, physics, life sciences, agriculture, public health, botany, medical sciences etc. One of the main objectives of the environmental chemistry is to determine the nature as well as quantity of specific pollutants in the environment. Pollutant (contaminant) is a substance that has a detrimental impact on the surrounding environment. [1]

The word pollution has been derived from the Latin word "Pollutionem" (meaning to defile or make dirty). Pollutant is a substance, the presence of which causes pollution. The pollution reaches through the air we breathe, the water we drink, the food we eat and the sound we hear.[2] Pollution is a substance which has the potential to induce cancer, tumor, Neoplastic effects, or to induce permanent transmissible change in the characteristic, if they are exposed to it via respiratory tract, skin, eyes, mouth or any other routes in quantity which is reasonable for them.

Water pollution results from the natural phenomenon as well as by human activities. It is an old age problem. About 70% of rivers and streams, not only of India but all over the world contains polluted water.[3]

Fluoride is a major worldwide pollutant. It has poisoned livestock and humans as well as lakes and streams. There is no question that fluoride is a toxic substance, which readily enters the body and has wide range of systematic effects. The developed and developing nations are adding literally hundreds of tons of fluoride to the water and contaminating the entire ecology of the plant. The four elements fluorine, chlorine, bromine and iodine together form a remarkable family.

Fluorine is known to be the most chemically active element. It is fairly widely distributed in nature and occurs in continental rocks in combined state. The fluorine is commonly present in igneous rocks in small quantities. J.H.L Vogt [4] estimated that fluorine is most abundant in acidic rocks. More than a hundred fluorine containing minerals have been identified. The most characteristic minerals containing fluorine are "fluorspar", flour or fluorite. Fluorine is also contained in some phosphates e.g., topaz, tourmaline, herderite, amphiboles, kodolite and in many other silicate minerals. Fluoride occurs in all-natural water supplies. It may be present in detrimental concern in "ground water". Fluoride largely occur in chemical wastes from industries.

Fluoride present in small concentration up to 1ppm are generally considered to be beneficial in water. Such water found to improve dental health and prevent the formation of dental carries. It is found that the fluoride concentration greater than 1ppm and excessive fluoride in drinking water may causes mottling of teeth or dental fluorosis which results in discoloration of enamel and chipping of teeth in severe cases.

Bone fluorosis and crippling effects are observed in the case where the concentration of fluoride exceeds 1.0mg/l. The presence of fluoride is determined by adding coloring agents and comparing with standard coloring solutions.

The reaction of fluoride with teeth enamel is ionic in nature and hence any fluoride compound that is capable of giving fluoride ions in dilute solution will give satisfactory results. The process of fluoridation is aimed to improve physical comfort with

respect to dental carries of the people consuming such water. Fluoridation may be carried out by applying fluorides in water either in the solution form or in powder form depending upon the characteristics of the fluorides to be used for fluoridation. The excess of fluoride if any can be removed by defluoridation.

Although fluorine is almost entirely disseminated in nature in the combined form.Its occurrence is associated with the presence of radioactivity as in classical case of wolsendorf fluorspar.[5] A Canadianfluorspar [6], the radioactivity of which has been measured, was found to contain 15-16 ppm of free fluorine. This radioactivity is attributed to the presence of radium, extracted from uranium minerals by fluorine containing water. On the other hand, the coloration of Russian fluorspar has been attributed to free calcium.[7]

According to National Research Council of U.S.A, 8 to 51% and sometimes as many as 80% of the children growing up in areas where ground water contains one part per million (1ppm) have dental fluorosis. Fluorosis is a permanent damage to the enamel which consist of white or brown spots that appear on the children teeth. India, China,Turkey where water is naturally high in fluoride residents tend to die before the age of 50, weak, arthritic and hunch backed. They drag themselves round leaning on sticks, their bones shatter like glass when they fall.[8]

W.H.O in 1987 conducted a correlation study between the registered cancer in communities in U.S.A and the fluoridation, from the significant correlation it was concluded that fluoride may not be the initiator but a promoter of cancer.[9]

The existence of fluoride bearing ground waters in India have been reported earlier by shrott and others in 1937.[10] Srinivasan [11] listed 37 places in India where the water had excessive soluble fluorides. In India there are more than 15 states where more than 50% of the districts are affected by high fluoride content in ground water. Among these severely affected states are Andhra Pradesh, Rajasthan, Tamil Nadu and Uttar Pradesh.

Various low-cost materials like Kaolinite, charfines, lignite and nirmali seeds have been tried to access their capacity for the removal of fluorides from water by Batch adsorption studies.[12]

The order or removal of fluorides from test solution using low cost materials was bentonite>charfines>kaolinite>lignite>nirmali seeds.

Conventional method of removal of fluoride are based on addition of some chemical to ground water. The removal takes place by coagulation or adsorption or ion exchange process. Additive method includes the use of lime and alumina compounds for fluoride removal. Lime treatment is feasible, but addition of magnesium is required.[13] Theoretically lowest fluoride concentration attainable by lime is 8 ppm based on the solubility of calcium fluoride, however the reported equilibrium concentration of fluoride is usually in the range of 10-20 ppm.[14]

Saha [15] has suggested a two stages process to bring down fluoride concentration to 1.5 ppm. Thus, effluent containing fluoride ion is treated chemically to bring down the fluoride about 15 ppm by precipitation technique followed by complexation to further reduce it to 1.5 ppm using $AlCl_3$in the presence of $CaCl_2$. The complex contains both aluminium and calcium along with fluoride. It is relatively stable complex and does break rapidly giving higher fluoride concentration on dilution with water. This method of effluent treatment has been very useful to save fresh water for dilution.

The removal of fluoride from water by calcium salt is not directly dependent on pH but it is a function of the formation of carbonate species from bicarbonate ions and therefore fluoride removal is more efficient at pH 5 to 7 as compared to higher pH 8 to 11.

Advanced methods for removing pollutants like phenol, Hg, Na, P, Fluoride etc. include chemical coagulation, filteration, ion exchange, carbon absorption, reverse osmosis.

Some plants are also used for purification of polluted water such as Euchronia, spirodela, wolffia, lemna etc. The plants of Eichornia can reduce pollutants up to 80%.

Water sample were collected from Bilaspur district of Chhattisgarh in PET bottles of half litre size and closed tightly. Samples were collected and fluoride concentration in all the samples have been determined. Fluoride contents were determined by SPADNS (2-p-sulphophenylazo)-1,8-dihydroxy3,6-napthalene disulphonate was obtained from E-Merck and SRL.

Nitrate contents were determined by spectrophotometric method. Sulphate and chloride were determined by turbidimetric method. Phosphate were determined by molybdenum blue method. For all spectrophotometric determination, a Hitachi U2001 UV-Vis spectrophotometer fitted with thermostated cell holders was used. Total hardness was calculated from concentrations of Ca^{2+} and Mg^{2+} ions. Doubly distilled water was used for all purposes.

II. MATERIALS AND METHODS

(A). MATERIALS

i. Guar-Gum: The Guar-Gum powder for the analysis was procured from local industry of Bilaspur. Particle size 80-100 mesh, ash 1.07%, moisture 11.3%, acid insoluble fraction 5.6%, protein 6.5%, pH of 1% solution 7.5, gum content 75-76%.
ii. Starches: Commercially available maize starch was used for the analysis.
iii. Sawdust: The waste of saw mills engaged in the cutting and chopping of teak, shisham. And bonsom woods, was obtained from local industries.

(B). EQUIPMENTS

A digital pH meter "NAINA" 335 systronics was used to determine pH of the solution.
Spectrophotometric observations were obtained on an AIMIL- Make "spectrochem-MK II spectrophotometer.
Magnetic stirrers MLH manufactured by S.P. Scientific instruments were used in stirring.

(C). PREPARATION OF SOLUTION

(i). Stock Fluoride solution: 221.0 mg of anhydrous Sodium fluoride (NaF) was dissolved in distilled water and diluted to 1,000 ml. This gives 100 ppm of sodium fluoride solution.

Standard Fluoride solution: 100 ml of stock Fluoride solution was diluted to 1000 ml with distilled water. This gives 10 ppm solution.

(ii). SPADNS SOLUTION: SPADNS solution was prepared by dissolving 958 mg sodium-2-(parasulphophenylazo)-1,8- dihydroxy 3,6-napthalene di sulphonate(SPADNS) in distilled water and diluted to 500 ml.

(iii). ZIRCONYL-ACID REAGENT: 133 mg zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) was dissolved in about 250 ml of distilled water, 350 ml Conc. HCl was subsequently added to it. The solution was made up to 500 ml with distilled water.

(iv). Reference Solution: Reference solution was prepared by adding 10 ml SPADNS solution to 100 ml of distilled water, 7 ml conc. HCl diluted to 10 ml was added to the diluted SPADNS solution. The resulting solution was used for setting the instrument reference point.

(v). Sodium arsenite solution: Sodium arsenite solution was prepared by dissolving 5.0 gm sodium arsenite and diluted to 1 litre with distilled water.

(vi). Preparation of standard curve: Fluoride standards in the range of 0 to 1.40 mg/l by diluting appropriate quantities of standard fluoride solution to 50 ml, with distilled water. Pipette 5 ml each of SPADNS and Zirconyl reagent, to each standard and mix well. Set spectrophotometer to zero absorbance with the reference solution and obtain absorbance readings of standards immediately.

A calibration curve of fluoride solution was prepared by plotting the absorbance at 570nm. Against fluoride as 10, 20,40, 60, 80 and 100 ppm (Table -I).
SPADNS[16] method was used for the estimation of fluoride concentration.

TABLE- I
ABSORBANCE OF STANDARD FLUORIDE SOLUTION

S.NO.	Concentration (ppm)	O. D
1	10	0.105
2	20	0.096
3	40	0.084
4	60	0.069
5	80	0.055
6	100	0.041

(i). Aluminium hydroxide gel (HAG) preparation: -

6.6675 gms of Aluminium chloride was dissolved in 500 ml distilled water then it was slowly added to the excess of ammonia solution and stirred well to get a gel and then filter.

(ii). Aluminium hydroxide guar gum gel (HAGG) preparation: -

6.6675 gms of Aluminium chloride was dissolved in 500 ml distilled water then it was slowly added to the excess of ammonia solution and stirred well to get a gel and then filter. This gel is homogenized with guar-gum (cross linked) 4:1 ratio and dry it about 123°in oven for about 6 hours. This is called as Aluminium hydroxide guar-gum gel.

III. DEFLUORIDATION BY HYDROUS ALUMINIUM GUAR-GELS AND DERIVATIVES: -

A large amount of industrial effluent containing fluoride is being generated these days from high-tech industries such as those manufacturing semiconductors and integrated circuits. Conventional methods for the removal of fluoride can be divided into two categories, those based on the addition of some chemicals to waste water during coagulation process and those based on the adsorption or ion exchange process.

Additive method includes the use of lime and aluminium compounds for the removal of fluoride. Lime treatment is feasible but it requires the addition of magnesium. [13,14] further the lowest fluoride concentration attainable by lime is 8 ppm, based on the solubility of calcium fluoride. The removal of fluoride with aluminium sulphate is feasible, but required dosages are very high, this causes the sludge disposal problem. Activated alumina is the commonly used adsorbent for removing fluoride. [17,18] By adsorption the fluoride concentration in the water can be brought to less than 1 ppm. The adsorption method involves passage of waste water or ground water through a contact bed, where fluoride is removed by ion exchange or adsorption process.

The experiment was planned with pure sodium fluoride solution and also from natural ground water containing fluoride from Bilaspur district of Chhattisgarh.

Investigation was also made with aluminium hydroxide gel impregnated on cross linked guar, starch and micro crystalline cellulose.

IV. HYDROUS ALUMINIUM GUAR GEL (HAGG)

The values of distribution coefficient (Kd), obtained from the sorption and desorption of fluoride ions at pH 3, 4, 5, 8 and 9 on HAGG have been given in Table II.

TABLE-II

Initial O.D – 0.040 Temperature – 30°
Wavelength – 570 nm
Volume – 100 ml

S.NO.	$[F]_i$ gdm^{-3}	(pH)i	Amount of Gel g	(pH)f	O. D	$[F]_f$ Gdm^{-3}	% Removal	Kd
1	100	3.02	0.1	6.52	0.078	46	54	1173
2	100	3.02	0.2	6.78	0.084	36	64	888
3	100	4.02	0.1	6.52	0.074	51.5	45.5	941
4	100	4.02	0.2	6.79	0.079	45	55	611
5	100	5.02	0.2	6.59	0.075	53	47	886
6	100	5.02	0.2	6.59	0.075	50	50	500
7	100	8.01	0.1	8.79	0.066	66.5	36.5	503
8	100	8.01	0.2	8.76	0.074	52	48	461
9	100	9.04	0.1	9.53	0.063	66	34	515
10	100	9.04	0.2	9.51	0.065	65	35	269

Average Kd – 674

V. RESULT & DISCUSSION

The effect of pH on the adsorption of fluoride on HAGG was investigated at pH 3, 4, 5, 8 and 9 using HAGG dosage 1 and 2 g/litre. The results are given in table-II along with the Kd values. The results indicate that the percentage removal of fluoride increases with the decrease in pH. The results indicate that the adsorption of fluoride on HAGG is maximum at pH 3 and decreased as the pH increased. This can be attributed to the neutralization of partial negative charge on the guar derivatives.

The mechanism of adsorption may be considered as the mixed effect of the classical and chromatographic adsorption. The improved adsorption at lower pH may be explained on the basis of anionic nature of the adsorbent. Further during the derivatization i.e., cross linking of the water-soluble guar gum some negatively charged sites may get introduced on it. Thus, there exists an anionic repulsion between the partial negative charge on the adsorbent surface and the fluoride ions. Thus, fluoride in the entire range of pH. In the lower range pH, the ionization of functional group such as -OH, -COOH on the guar gum are first suppressed

and then gets protonated which facilitates the migration of fluoride ion from the liquid medium to the solid guar gum surface and keeps the fluoride ion bound to it by electrostatic force of attraction and hydrogen bonding etc. Therefore, an improved adsorption at lower pH is obtained.

VI. CONCLUSION

Defluoridation of ground water by hydrous aluminum guar gel is pH dependent and the mechanism of adsorption at lower pH gives improved results. Therefore, an improved adsorption at lower pH is obtained.

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